OFFICE OF NAVAL RESEARCH

CONTRACT N00014-89-J-1849

R & T Code 4134005

Technical Report No. 3

PREPARATION AND CHARACTERIZATION OF ALUMINA FILMS PREPARED BY A NOVEL SPRAY PYROLYSIS METHOD

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Prepared for Publication in

MATERIALS RESEARCH BULLETIN

January 15, 1990

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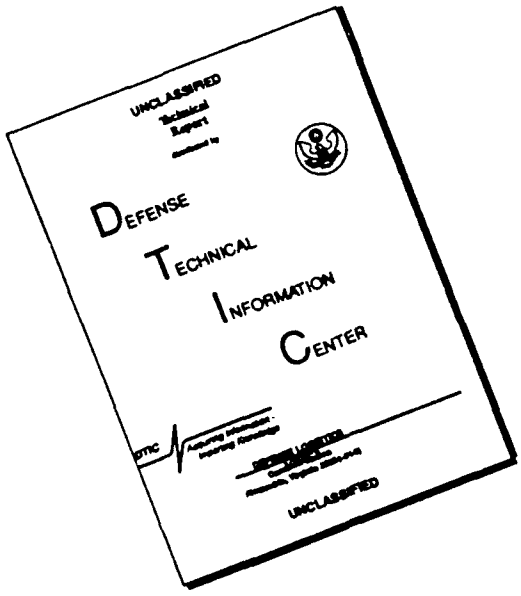

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4 PERFORMING ORGANIZATION REPORT NUMBER(S) **# 3**	5 MONITORING ORGANIZATION REPORT NUMBER(S) **N000 14-89-J-1849**
6a NAME OF PERFORMING ORGANIZATION **BROWN UNIVERSITY** **AARON WOLD** 6b OFFICE SYMBOL *(If applicable)*	7a NAME OF MONITORING ORGANIZATION **OFFICE OF NAVAL RESEARCH**
6c ADDRESS *(City, State, and ZIP Code)* **DEPARTMENT OF CHEMISTRY** **PROVIDENCE, RI 02912**	7b ADDRESS *(City, State, and ZIP Code)* **800 N. QUINCY STREET** **ARLINGTON, VA 22217**
8a NAME OF FUNDING / SPONSORING ORGANIZATION 8b OFFICE SYMBOL *(If applicable)*	9 PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER
8c ADDRESS *(City, State, and ZIP Code)*	10 SOURCE OF FUNDING NUMBERS PROGRAM ELEMENT NO / PROJECT NO / TASK NO / WORK UNIT NO

11 TITLE *(Include Security Classification)*

Preparation and characterization of alumina films prepared by a novel spray pyrolysis method.

12 PERSONAL AUTHOR(S)

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13a TYPE OF REPORT	13b TIME COVERED	14 DATE OF REPORT *(Year, Month, Day)*	15 PAGE COUNT
Technical	FROM _____ TO _____	**January 15, 1990**	**8**

16 SUPPLEMENTARY NOTATION

PREPARED FOR PUBLICATION IN MATERIALS RESEARCH BULLETIN

17 COSATI CODES			18 SUBJECT TERMS *(Continue on reverse if necessary and identify by block number)*
FIELD	GROUP	SUB-GROUP	

19 ABSTRACT *(Continue on reverse if necessary and identify by block number)*

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20 DISTRIBUTION / AVAILABILITY OF ABSTRACT	21 ABSTRACT SECURITY CLASSIFICATION
☐ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT ☐ DTIC USERS	
22a NAME OF RESPONSIBLE INDIVIDUAL	22b TELEPHONE *(Include Area Code)* / 22c OFFICE SYMBOL

DD FORM 1473, 84 MAR 83 APR edition may be used until exhausted
All other editions are obsolete

SECURITY CLASSIFICATION OF THIS PAGE

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ABSTRACT

Alumina thin films of 2000 A were deposited on n-type silicon wafers by a novel spray pyrolysis method. The spray solution contained an aluminum acetylacetonato complex which was characterized by NMR techniques. The deposited films of Al_2O_3 were homogeneous, uniform, dense and had breakdown potentials of greater than 10 V.
MATERIALS INDEX: Alumina; Thin films; Spray pyrolysis.

Introduction

Aluminum oxide is an attractive candidate for thin insulating layers in electronic devices because of its high dielectric constant, low sensitivity to Na^+ diffusion and high radiation resistance. These films would be useful for numerous applications including surface protection and selective masking during diffusion, in device isolation masking against impurities, junction passivation, and insulation between metal layers.

Earlier efforts to prepare homogeneous films of Al_2O_3 on an InP support by a sol-gel method indicated that such films would be porous and result in low breakdown potentials (7). Several investigators have reported the preparation of Al_2O_3 films on various semiconductors by the thermal decomposition of aluminum isopropoxide (8-11). Fournier, et al. (11) reported Al_2O_3 films with breakdown voltages of 4 V.

Other low temperature preparative methods of thin film insulators need to be investigated and the resulting films compared as to uniformity, homogeneity and electrical properties. Among the alternative methods, spray pyrolysis processing has been shown to be a relatively inexpensive method for the preparation of oxide films (12). Such films include In_2O_3, SnO_2, Fe_2O_3, Cr_2O_3 and Al_2O_3 (12,13). A novel spray pyrolysis process has recently been developed for the preparation of thin oxide films of high quality (14,15). It was the purpose of this work to investigate the preparation and properties of thin Al_2O_3 films on semiconductor substrates deposited by this spray pyrolysis method. The alumina films were prepared by ultrasonically spraying and thermally decomposing an aqueous aluminum acetylacetonate solution onto silicon substrates at low temperatures. The films were characterized by ellipsometry, electron microscopy and dc voltage breakdown measurements.

Experimental

Solution Preparation

3.75 g (0.01 mole) of aluminum nitrate nonahydrate (Baker Reagent) was dissolved in 15 ml of distilled water and 10 ml of methanol. This solution was immersed in an ice bath with constant stirring and 3 ml of acetylacetone (Aldrich) and 4 ml of propylene oxide (Aldrich) were added to the solution. Concentrated ammonium hydroxide was added to the solution dropwise until the pH was approximately 7 and a fluffy white precipitate of $Al(acac)_3$ was formed. The precipitate and solution were refrigerated overnight, filtered and dried.

Approximately 200 ml of distilled water were added to 0.92 g of aluminum acetylacetonate in a 250 ml volumetric flask. It was then found necessary to add 4 ml of concentrated acetic acid to the flask in order to dissolve the aluminum compound. The remaining volume in the flask was filled with distilled water giving a solution which was 0.01 M in Al^{3+}.

NMR Characterization of Aluminum Acetylactonate Solution

General. Proton and aluminum NMR spectra were recorded on Bruker WM 250 MHz and Bruker AM 400 MHz instruments with proton resonance frequencies of 250.13 MHz and 400.13 MHz, respectively, and aluminum 27 resonance frequencies of 65.132 MHz and 104.13 MHz, respectively. DSS (or 2,2-dimethyl-2-silapentane-5-sulfonic acid, Na^+ salt) in D_2O was used as an external reference for the proton NMR. Hexaaquoaluminum(III) $[Al(H_2O)_6]^{3+}$ in D_2O was used as an external reference for the ^{27}Al-NMR (16).

Sample Solutions. Eight ml of deuterium oxide (Cambridge Isotope Labs) were added to 0.405 g aluminum acetylacetonate in a 10 ml volumetric flask. Then, 0.016 ml d^4-acetic acid (Aldrich) were added and the flask was filled to volume with deuterium oxide. An analogous solution was prepared using normal acetic acid. A saturated solution of aluminum acetylacetonate in $CDCl_3$ (Cambridge) was also prepared.

Preparation of Al_2O_3 Films

Deposition of alumina was performed by ultrasonically nebulizing, spraying and thermally decomposing the aluminum acetylacetonate solution in oxygen at 430°C in the reactor shown in Fig. 1. The reactor was heated by a two-zone mirror furnace (Trans-Temp, Chelsea, MA). The solution was nebulized by a commercial ultrasonic humidifier (Holmes Air) and was carried into the reactor by oxygen. A typical set of reaction parameters is shown in Table 1. The nebulized solution was delivered to the substrate in 5 sec pulses with 20 sec intervals between pulses. In addition, the oxygen carrier gas was allowed to flow continuously in order to minimize temperature fluctuation during spray pulsing. The substrates consisted of 1 cm squares of n-type (100) silicon with resistivities of 0.01 Ω-cm and 8 Ω-cm.

Table 1: Reaction Parameters

Substrate Temperature	430	°C
Sweep flow rate	3.5	l/min
Nozzle-substrate distance	8.3	cm
Cycle time	25	sec
Nebulization time	5	sec
No. of cycles	250	

Cleaning and etching of the silicon substrates were carried out just prior to deposition according to the procedure described by Fournier, et al. (11).

Film Characterization

The thickness of the films was determined by ellipsometry using a Rudolph Research Auto EL-II ellipsometer. The wavelength of the laser beam was 632.8 nm. Values of the two ellipsometric angles, delta and psi, were recorded and input to a Hewlett Packard 9825A computer to calculate the thickness. Additional input parameters for thickness calculation were the real (n_s = 3.877) and complex (k_s = 0.019) values for the index of refraction of the substrate and a trial value for the index of refraction of the film (n_p = 1.5); the values are taken from the data of Aspnes and Studna (17).

The infrared spectra was obtained using a Bomen (Model No. BA3.02) FTIR Spectrometer with a mercury cadmium telluride detector. Measurements were made on both coated and uncoated silicon substrates. The final data were obtained from the ratio of these measurements. The plotted output corresponds to the properties of the film.

Characterization of the surface topography was achieved by examining replicas of the surface in a Philips Optics Electron Microscope (420 STEM). A replication solution (Ladd) was applied to the surface of the film and allowed to dry. Carbon-platinum was shadow evaporated onto the stripped plastic at an angle of 60°; the overall thickness of the replica was 250 Å. The carbon replicas were liberated using acetone and mounted on 200 mesh copper grids. Magnification calibration consisted of photographing spherical particles of known diameter (0.312 μm).

Electrodes for the DC current-voltage measurements consisted of indium alloy (Indalloy #9, Indium Corporation of America) ultrasonically bonded to the back surface of the silicon substrate. Gold was evaporated through a mask to obtain an array of circular electrodes of area 1.1 mm^2 on the surface of the alumina film. The indium alloy contacts were checked for ohmic behavior before measurement of the DC current-voltage behavior. Contact to a gold electrode was obtained by touching a gold tipped micromanipulator to the surface. Samples were checked with the gold positively and negatively biased; the reported DC current-voltage behavior is that for the gold electrode made positive with respect to the substrate. The area measured ignores a 1 mm boundary along the substrate edge. A DC potential was applied via a voltage follower having an output impedance less than 0.1 Ω, and the resulting response was measured with a current amplifier, which inserted a negligible potential drop (less than 1 microvolt) in the external circuit.

Results and Discussion

^{1}H-NMR

In the $Al(acac)_3$ solution in D_2O with d^4-acetic acid, two strong peaks, with the approximate intensity ratio 2:1, were observed with chemical shifts, δ, at 4.61 and 2.03 ppm. Also, a broad HDO peak at 1.82 ppm was seen. It was assumed that some of the acetylacetonate ligands on the aluminum acetylacetonate were replaced so that there would be free acetylacetone and bound acetylacetonate. The two strong peaks represent the methyl groups of bound $acac^-$ and free acetylacetone (presumably both keto and enol forms in

equilibrium). The NMR data in the literature are not consistent (12-20) so definite assignment of these peak positions was not feasible. The fraction of enol is 0.170 (21); however, a separate line for enol was not found. The hydrogens of the methylene group exchange with deuterium, and hence, a peak position of methylene in either free or bound acetylacetone could not be found.

In an analogous solution with normal acetic acid, the methyl peak for acetic acid/acetate ion (pH = 2.6) at δ = 2.22 was very broad, $w_{\frac{1}{2}}$ = 288Hz (probably due to exchange processes). A small subsidiary peak at δ = 1.84 ppm was found, which is assigned to aluminum bound acetate ion. Exact mole ratios could not be determined because complete separation of peaks was not achieved. Nevertheless, these spectra are strong, if not conclusive, evidence that some acetate ion is attached to aluminum ion and is exchanging.

^{27}Al-NMR

The isotope ^{27}Al has 100% abundance. It is a quadrupolar nucleus with spin I = 5/2 and a quadrupolar moment Q = 0.149 barns (22-24). The reference species is $[Al(H_2O)_6]^{3+}$ (δ = 0.000 ppm). The ^{27}Al resonance in the D_2O solution was at δ = 0.216 ppm, indicating that there is near octahedral symmetry with ligands acac$^-$, $CH_3CO_2^-$ and D_2O. The $Al(acac)_3$ shift in $CDCl_3$ was not compared because of the different solvent system.

A purely octahedral complex such as $[Al(H_2O)_6]^{3+}$ should have a very narrow line (about 2 Hz) due to the cubic symmetry. A less symmetric complex, even with six oxygen ligands, should have a broader line because of the quadrupole moment with a non-zero electric field gradient. For example, $Al(acac)_3$ with a trigonal distortion has a line width of 116 Hz in $CDCl_3$. In our solution (D_2O with 0.3M acetic acid), the line width was 433 Hz. This very large width indicates that at least one acetylacetonate ligand has been replaced by water and/or acetate ion.

Preparation and Characterization of Films

The spray pyrolysis reactor gave alumina films of approximately 2000 Å thickness on silicon using the deposition conditions given in Table 1. The substrate-nozzle distance was the most critical parameter for obtaining uniform films. At shorter distances the films were thicker in the center and at longer distances the films were thicker along the edges. This non-uniformity could be observed when moving 3 mm away from the optimum distance. The substrate temperature was kept relatively low in order for further investigation of deposition of these films on III-V semiconductors.

The alumina films appeared smooth and had a homogeneous straw yellow color. Viguie and Spitz (25) identified several growth mechanisms for films prepared by spray pyrolysis as a function of substrate temperature. They indicated that the best films are obtained when the complex metal salt volatilizes and the vapor deposits directly on the substrate. The Al_2O_3 films grown in this study are probably deposited from a vapor phase because of the smooth, shiny and mirror-like appearance. This is consistent with the NMR investigation studies which were carried out in order to determine the composition of the aluminum acetylacetonate species which is formed in dilute acetic acid.

The thickness of a number of films was measured at different positions on the substrate with an ellipsometer. It was found that the thickness was

1. Furnace
2. Substrate rotating motor
3. Substrate
4. Spray nozzle
5. Oxygen flow
6. Solution
7. Membrane
8. Ultrasonic humidifier

Fig. 1. Schematic of spray pyrolysis reactor

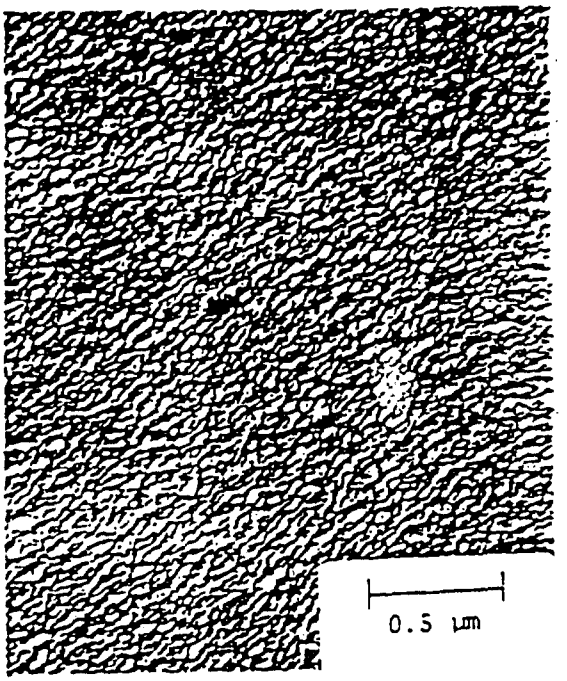

Fig. 2. Photomicrograph of a replica of the film surface at 37,000 X.

uniform to within 1% except near the very edge. The bright and uniform color also revealed that the films were of uniform thickness. From the IR data, there was no absorption band from 2700 - 3700 cm^{-1} which is characteristic of an OH group, thus indicating no residual hydration in the films. This absorption band was seen in films prepared by MOCVD below 400°C (11). A photomicrograph of a replica of the surface of an alumina film is shown in Fig. 2. The film appears to be homogeneous, pin-hole free and is comprised of densely packed small particles. The particle size is approximately 300-400 Å.

DC current-voltage measurements were made on several films approximately 2000 A thick. There was no observed voltage breakdown up to 10 V of applied potential. These results are consistent with the IR data and the electron micrographs which indicate the formation of relatively pin-hole free, dense alumina films on silicon substrates. Films prepared by thermal decomposition of aluminum isopropoxide (11) had voltage breakdowns of 4 V even in films grown at higher temperatures (500°C).

Conclusions

It is concluded that alumina films grown by thermally decomposing an ultrasonically nebulized aqueous acetic acid solution of aluminum acetylacetonate results in more dense and pin-hole free films with higher dc breakdown voltages than obtained by MOCVD or sol-gel deposition. The ^{1}H and ^{27}Al NMR studies indicate that some of the acetylacetanato ligands have been replaced by water and/or acetate ion. The remaining bidentate ligands may help to keep the aluminum in homogeneous solution and provide volatility of the species when sprayed.

Acknowledgments

This research was partially supported by the Office of Naval Research, by National Science Foundation Grant No. DMR 8901270, by GTE Labs. Inc. Waltham, MA, and by Eastman Kodak Company, Rochester, NY.

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